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A

Cyclic Isolongifolanone-Ketals -

their manufacture and their application

SLY 4/93 P Today  
Nowadays, industrially manufactured perfume oils consist of synthetic odorants largely. The traditional application of essential oils or extracts of vegetable or animal origin is now mainly restricted to the area of alcoholic perfumery. Perfume for detergents, soaps, household cleaners and similar products requires the use of odorants which meet the technical demands of stability and substantivity. To comply with these demands, perfumes which are used in technical consumer products are essentially composed of synthetic odorants. Because these perfume oils are needed in large quantities as a result all major perfume companies and manufacturers of aroma chemicals have dedicated their research work over the last decades to produce new aroma chemicals.

c  
B c  
It has become increasingly <sup>apparent</sup> ~~apparent~~ during the last 10 years that synthetic odorants which were originally <sup>destined</sup> ~~destinated~~ for the technical perfumery, and which due to their low prices and high stability were accordingly ~~positioned in the market~~ are now more and more used in the alcoholic perfumery. Perfumers have used their perfumistic know-how gained from the use of synthetic aroma chemicals in technical perfumes, and applied it also to alcoholic perfumery as aesthetic chances <sup>today</sup> ~~may allow~~ ~~Nowadays~~, a successfull new aroma chemical has to meet the following demands:

2

1. it has to present a high olfactory and aesthetic value and must be applicable in as wide a range of fragrance products as possible;
2. it has to be stable in most technical applications;
3. it has to show a good value-/for money-ratio;
4. it should be manufactured from generally available raw materials from renewable resources, whenever possible.

Such a raw material of natural origin available in large quantities is Longifolene (1) which is to be found as a main component in the Indian oil of turpentine and as a minor component in many other turpentine oils and other essential oils.

About 20 years ago, research laboratories of the aroma chemical industry produced a number of derivative products from Longifolene, which had odorant qualities. As reported in a summary by G. Ohloff in his book "Riechstoffe und Geruchssinn" (Springer-Verlag, Berlin, 1990, ISBN-Nr. 3-540-52560-2, pages 87-88) at least 4 commercial odorants are derived from the Longifolene (1). The Isolongifolene (2) which is obtained by the isomerization of Longifolene (1) can be proved to have fathered 13 commercial products.

The chemistry and olfactory qualities of derivatives of the Isolongifolene (2) are summarized by G. Färber and H. Tan:

"Riechstoffe aus Isolongifolen", G. Färber, Parfümerie & Kosmetik, 68, 18 (1987)

"Der Gebrauch von Riechstoffen aus Isolongifolenen in der Parfümerie", H. Tan, Parfümerie & Kosmetik, 67, 564 (1986)

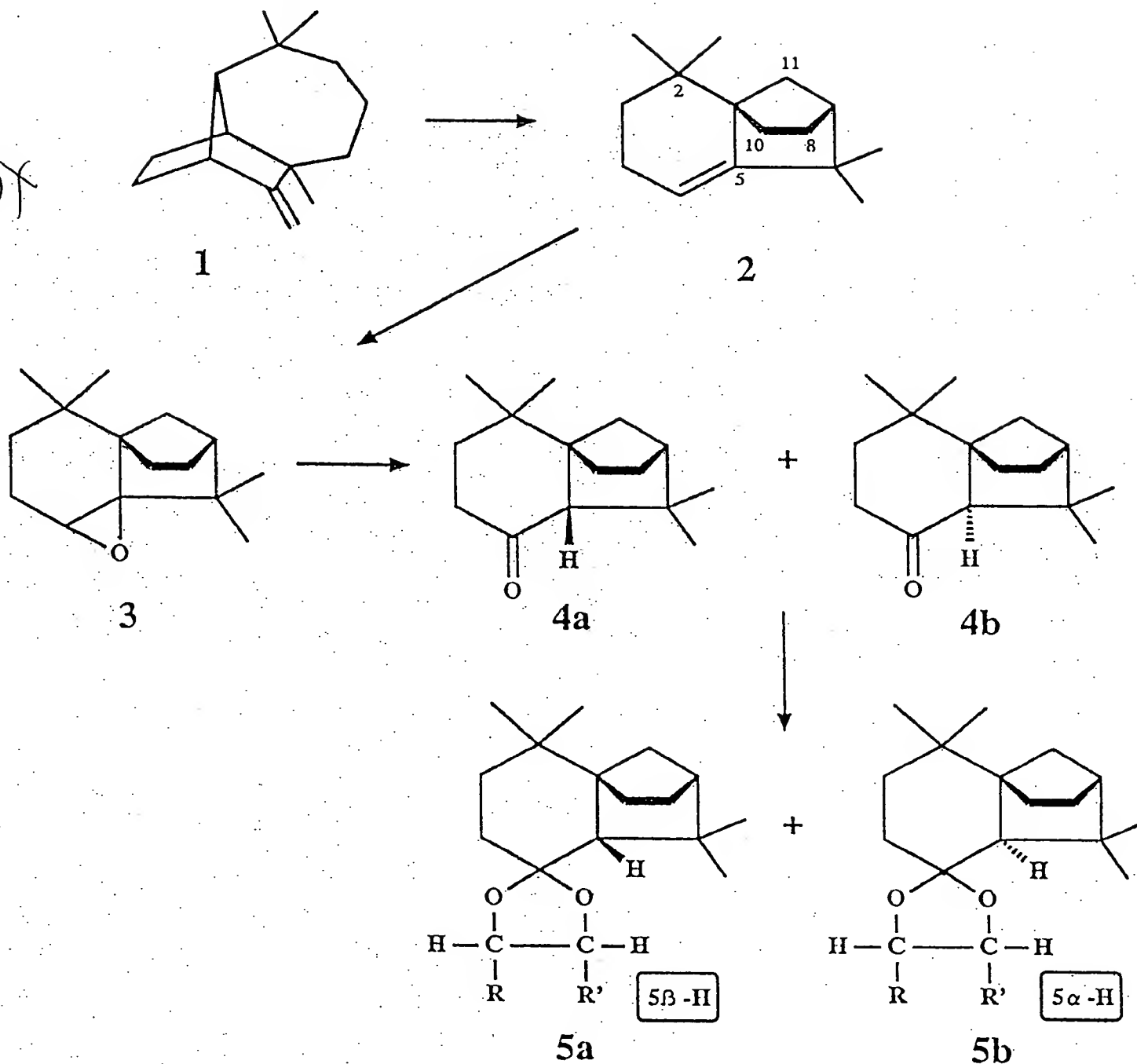
The derivatives of Isolongifolene (2) obtained by epoxidation, Prins-reaction (reaction with formaldehyde) or allylic oxidation are considered olfactorily more valuable than the derivatives of Longifolene (1). They (2) are odorants of a warm-woody odor type, with some little amberlike aspects (Ohloff loc. cit.).

↓  
L The epoxide (3) obtained by the reaction of Isolongifolene with peracids can be transferred as is known into mixtures of epimer ketones. The ketone mixtures may contain different proportions of isomers with different odor effects. The ketone **4a** is preferably manufactured in kinetic reaction while the ketone **4b** is the thermodynamically more stable epimer.

According to the state of the art as described above, this area of the aroma chemical chemistry is considered to be especially well researched. Together with the derivatives of Longifolene and Isolongifolene which have useful odor qualities, a large number of other derivatives are known with little or no such value.

4

150x



5a	R=H	R'=H	5b
6a	R=H	R'=Me	6b
6c	R=Me	R'=H	6d
7a	R=H	R'=Et	7b
7c	R=Et	R'=H	7d
8a } 8c }	R=Me ( $\alpha, \beta$ ) R'=Me ( $\alpha, \beta$ )		8b 8d

57

P  
C  
C  
It is all the more surprising therefore, that new valuable odorants could be found in the area of the Longifolene derivatives such as the herewith claimed new cyclic ~~acetals~~<sup>acetals</sup> of the general formula A. The ~~acetals~~<sup>acetals</sup> of the general formula A present unique olfactory qualities clearly standing out from the known odorants derivated from Isolongifolene (2) and superior to them. The new compounds of the general formula A present strongly woody olfactory qualities with flowery-fresh effects and with a velvety moss/ambra accent (see example 1); they are especially long-lasting and act as fixatives.

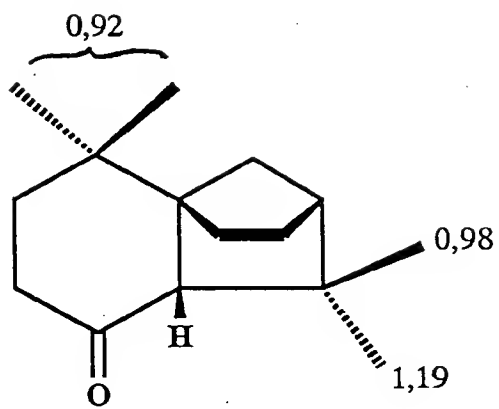
I  
I  
G  
For the manufacture of compounds of the general formula A, Longifolene (1) has been treated as is well known with a mixture of acetic acid and sulphuric acid [U.R. Nayak, S. Dev, Tetrahedron 8, 42-48 (1960)] or with boron trifluoride-etherate [R.E. Beyler, G. Ourisson, J.Org.Chem. 30, 2838-2839 (1965)] to obtain Isolongifolene (2) by isomerization. The epoxide (3) [L.K. Lala, J.B. Hall, J.Org.Chem. 35, 1172, (1970); J.R. Prahlad, R. Ranganathan, W. Ramdas Nayak, T.S. Santhanakrishnan, S. Dev, Tetrahedron Lett. 8, 417 (1964)] obtained by epoxidation of Isolongifolene (2) has been transformed, as is well known, into the mixture of the epimer ketones **4a/4b** [R. Ranganathan, U.R. Nayak, T.S. Santhanakrishnan, S. Dev, Tetrahedron 26, 621 (1970)]. In known conditions of the kinetic reaction the ring-opening of the epoxide produced a mixture of ketones **4a/4b** concentrated in **4a** (see example 2 = 96 : 4).

It is known that **4a** will be isomerized into the thermodynamically more stable ketone **4b** under the influence of basic catalysts or by heating. Depending on the conditions of the reaction, mixtures of equilibrium of **4a/4b** are obtained [L.K. Lala, J. Org. Chem. 36, 2560-2561 (1971)].

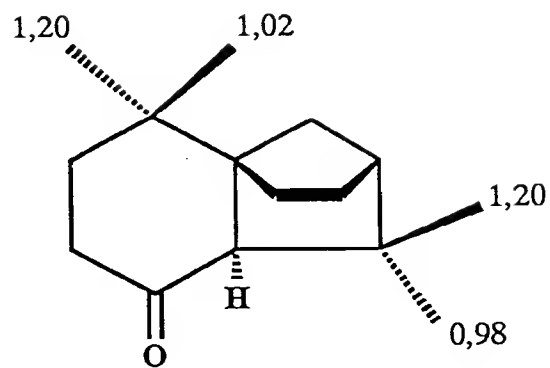
Our example 3 shows an isomerization not yet described to date leading from a mixture of ketones **4a/4b** (96:4) to a specially highly concentrated mixture of equilibrium **4a/4b** (9:91). The ketones **4a/4b** have been isolated by distillation and chromatography and spectroscopically characterized. [C.W. Greengrass, R. Ramage, Tetrahedron 31, 689-694 (1975)].

From ketones **4a**, **4b** which were present purely or in high concentration or in mixtures of equilibrium the new cyclic acetals of the formula **A** are produced as is known by the reaction with aliphatic 1,2-dioles in acidic catalysis with separation of water. The separation of water is preferably realized at boiling point with suitable inert solvents as carriers (examples 5 - 10).

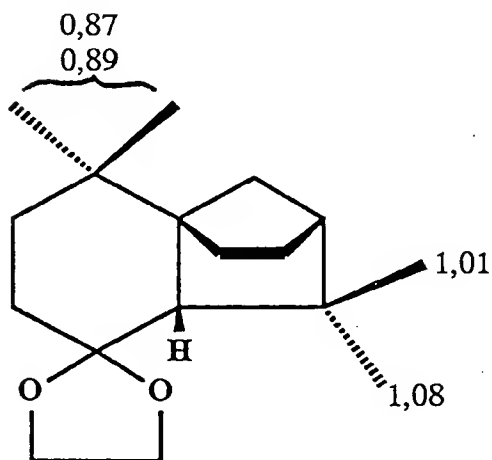
If different solvents - toluene, cyclohexane, benzene fractions or n-pentane - are applied, the epimer ketals are produced in different proportions (example 5). So from **4a/4b** (86:14) in example 2 under the effect of ethylene glycol in toluene the ketals **5a/5b** have been obtained in the ratio of 3:2. When using n-pentane a ketal mixture **5a/5b** was obtained after even a markedly prolonged reaction period. The ketals of formula **A** can be separated alternatively by distillation of the starting material **4a/4b** if need be.



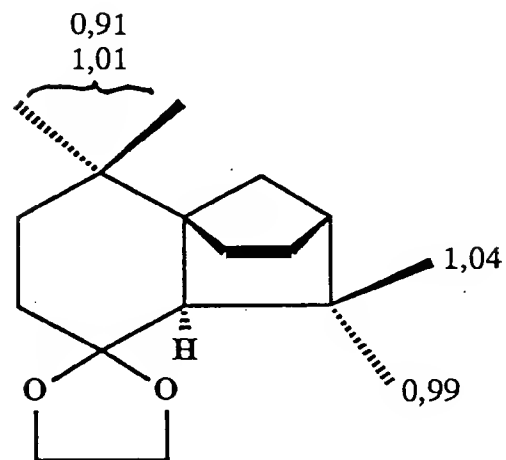
4a



4b



5a



5b

**1H-NMR-Data,  $\delta$  [ppm]**

8

PD The mixture equilibrated by basic catalysis of ketones **4a/4b** (9:91, in example 3) had to undergo ketalisation reactions as well. Depending on the solvent used, different mixtures of **5a/5b** were obtained, but which differed from the ketal mixtures **5a/5b** obtained from the ketone mixtures **4a/4b** (86:14, of example 2) so far as their relative concentrations were concerned. This varying reaction may be understood as kinetically controlled reaction during during the ketalisation.

Analogue to the ketals **5a/5b** the ketals **6a/6b/6c/6d** were obtained by reaction of **4a/4b** with 1,2-propandiol, the ketals **7a/7b/7c/7d** with 1,2-butandiol, the ketals **8a/8b/8c/8d** with 2,3-butandiol - each of them as a mixture. The methyl- or ethyl groups of the ketal radical may appear in an  $\alpha$ - or  $\beta$ -configuration.

162 The compounds **5a**, **6a**, **6c**, **7a**, **7c**, **8a**, **8c** are established as  $\beta$ -configured; the compounds **5b**, **6b**, **6d**, **7b**, **7d**, **8b**, **8d** as  $\alpha$ -configured. Because starting from (+)-Longifolene the chiral ketals of the general formula **A** were obtained by means of the chiral ketones **4a/4b**; **4a/4b** exist as a mixture of epimers (**5a/5b**), respectively as diastereo ~~isomers~~ <sup>isomers</sup>. **6a/6b** and **7a/7b** are constitutionally isomer to **6c/6d**, respectively **7c/7d**. Starting from (-)-Longifolene each of the enantiomer compounds **5a,b** - **8a-d** are accessible.



Since both the composition of the ketal mixtures depends on the conditions of the reaction (example 5), and, the single diastereo isomers may be obtained in purity (examples 6, 7), the proportions within the mixtures may be adjusted to any level.

14  
L  
1H The attribution of the structure of the new compounds 5 - 8 has been based on the spectroscopical results (examples 5 - 10). The 1H-NMR-spectra of the compounds 5a, 5b (designs 1, 2) have been interpreted in analogy to the attributions given by C.W. Green-grass and R. Ramage, Tetrahedron 31, 689 (19758) for the ketones 4a, 4b.

The new compounds of the formula A are well suited as odorants due to their olfactory qualities and their stability. They may be used successfully for perfume compositions of any fragrance type either as a main component or in traces to good avail. The examples quoted may not be understood as limitations.

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DEU  
EXAMPLE 1

Manufacture of Isolongifolene (2)

P  
60H  
Over a period of 30 minutes 240 g (0.79 mol) of Longifolene (1) (80 % ex Indian oil of turpentine  $[\alpha]_D = + 39.4^\circ$ ) were dropped into a heated solution (60 °C) of 90 g toluene and 10 g (0.07 mol) BF<sub>3</sub>-etherate. This was stirred at 100 °C for 3 hours, than cooled down to room temperature and neutralized. After drying above Na<sub>2</sub>SO<sub>4</sub> the solvent was distilled at reduced pressure. A raw product of 198 g (of 70.2 % according to GLC) remained.

cl  
31  
*Gas chromatogram*  
~~Gas chromatogramme~~ (HP 5890, DBWAX-30 N, 30 m, 150 °C - 240 °C, 8 °C/min).

cl  
EXAMPLE 2

cl  
Manufacture of an Isolongifolanene mixture **4a/4b** (86:14)

P  
H  
14  
A threeneck-roundbottom-flask with jacketed coil condenser and dropping funnel was charged with 198 g (0.68 mol) Isolongifolene (2) (70.2 % according to GLC) from example 1 plus 80 g toluene and 68 g (1.48 mol) formic acid and heated at 60 - 70 °C. Into this was dropped over a period of 1 hour 136 g (1.4 mol) H<sub>2</sub>O<sub>2</sub> at 35 % concentration. After stirring for 3 hours at 80 - 85 °C it was

11

c  
I  
cooled to room temperature and worked up. The separated organic phase was neutralized with ~~sodium~~ <sup>sodium</sup> carbonate solution and water, dried above Na<sub>2</sub>SO<sub>4</sub> and the solvent distilled at reduced pressure. 199 g raw product remained. GLC **4a** (71 %), **4b** (2.5 %) [96:4].

I 14  
Distillation with a 15 cm Vigreux-column produced 165 g raw product of **4a/4b**; b.p.<sub>2mm</sub> 120 - 153 °C. GLC: **4a** (74 %), **4b** (3 %).

I 14  
L  
A subsequent distillation with a column with metallic packing produced: 110 g **4a/4b** (74.4 % theoretical yield) b.p.<sub>2mm</sub> 137 - 141 °C; GC **4a** (77 %), **4b** (12.8 %) [86:14].

P  
D 20/4 = 1,0037

L  
n 20/D = 1,5006

L 6031 [α] 20/D = - 8,5°

Chuf Gas chromatogram  
~~Gaschromatogramme~~: Conditions see example 1

P 14  
I  
GLC/MS: HP 5970 DBWAX-60 N, 60 m 60, - 240 °C, 4°/min

**4a** Rt = 40,47'

MS: m/e (%) = 220 (100, M<sup>+</sup>), 205 (41), 191 (82), 177 (41),  
164 (62), 149 (50), 121 (56), 107 (40), 83 (27),  
55 (21), 41 (17).

12

P<sub>1</sub> 40  
L  
4b Rt = 41, 41'

MS: m/e (%) = 220 (69, M<sup>+</sup>), 205 (23), 191 (55), 177 (44),  
164 (100), 149 (55), 121 (53), 107 (37), 91 (21),  
55 (21), 41 (19).

CE  
CEX  
EXAMPLE 3

C-3-Epimerization of Isolongifolanone (4a/4b)

P<sub>1</sub>  
L  
880 g (4 mol) raw (undistilled) ketone mixture 4a/4b from example 2 (purity according to GLC: 4a (63.3 %), 4b (2.48 %) [96:4]; 750 g methanol, 40 g (0.5 mol) NaOH 50 % were charged into a three-neck-roundbottom-flask and stirred for 8 hours under reflux. After this period 30 g (0.5 mol) concentrated acetic acid were added to cool down to room temperature. After the distillation of the solvent at reduced pressure the residual was mixed with water. The organic phase was then separated. The waterphase was extracted with 100 ml benzene. The mixed organic phases were washed first with <sup>sodium</sup>~~sodium~~ carbonate solution, then with water and dried above Na<sub>2</sub>SO<sub>4</sub>. The solvent was distilled at reduced pressure. 860 g dark brown oil remained.

P<sub>1</sub>  
GLC: 4a (6.3 %), 4b (59.3 %) [9 : 91]

EXAMPLE 4

C-3-Epimerization of pure Isolongifolanone (4a/4b)

440 g (2 mol) purely distilled ketone mixture 4a/4b from example 2 [purity according to GLC: 4a (77 %), 4b (12.8 %) [86:14]; 400 ml methanol, 20 g (0.25 mol) NaOH 50 % were charged into a 2 l three-neck-roundbottom-flask and stirred for 5 hours under reflux. After cooling to room temperature, 15.5 g (0.25 mol) concentrated acetic acid were added; the solvent was distilled at reduced pressure. The residual was then mixed with water. The organic phase was separated and the ~~water phase~~ <sup>water phase</sup> was extracted with 100 ml benzene. The mixed organic phases were neutralized with ~~sodium~~ <sup>sodium</sup> carbonate solution and water; after concentration 430 g brown oil remained.

GLC: 4a (9.2 %), 4b (79.5 %) [1:9]

Distillation in a 15 cm Vigreux-column produced 411 g 4a/4b (b.p. 2mm 135 - 157 °C). The subsequent distillation in a 40 cm column with metallic packing produced 399 g (90.7 % theor. yield) 4a/4b b.p. 2mm 139 - 142 °C.

GLC: 4a (13.4 %), 4b (80.6 %) [14 : 86]

D 20/4 = 1.0042

n 20/D = 1.5007

[α] 20/D = - 34.7°

ce EXAMPLE 5

clg Reaction of Isolongifolanone **4a/4b** with ethylene glycol

Pg 220 g (0.6 mol) ketone mixture **4a/4b** from example 2, 3 or 4, 186 g  
14 (3 mol) ethylene glycol, 1 g p-toluene sulfonic acid plus 300 ml  
14 solvent (toluene, cyclohexane, benzene (63 - 80 °C), n-pentane)  
were charged in a 1 l three-neck-roundbottom-flask with water  
separator and heated at boiling point for 48 - 78 hours and stir-  
red with water separation. During the reaction about 20 ml water  
each were separated at each stage. After cooling to room tem-  
c perature, the mixture was neutralized with ~~sodium~~ <sup>sodium</sup> carbonate solu-  
tion and water, dried above Na<sub>2</sub>SO<sub>4</sub>, and the solvent distilled at  
14 reduced pressure. 245 - 265 g raw product of either yellow or  
brown oil respectively were obtained.

1 Distillation with a 15 cm Vigreux-column produced 230 g raw **4a/4b**  
14 (b.p., 68 - 170 °C). The subsequent distillation with a 40 cm  
column with metallic packing produced about 140 g (53 % theor.  
1 yield) **5a/5b** of light yellow oil.

793 Table  
Tabular 1 shows the results in a summary.

Products of the reaction of 4a/4b with ethylenglycol/p-toluenesulfonic acid

starting material (GLC-%) 4a + 4b [4a/4b]	Solvents	Reaction- -Temp. -Time	Composition of Product (GLC-%) 4a 4b 5a 5b [5a/5b]
a) 71 % 2.5 % [96: 4] 71 % 2.5 % [96: 4] 71 % 2.5 % [96: 4] (raw products from example 2)	Benzene (63-80°C) Cyclohexane Toluene	70-72°C 70 h 90-92°C 48 h 120 °C 24 h	7.2 3.8 53.6 2.2 [96: 4] 5.1 4.8 51.3 3.8 [93: 7] 1.2 10.4 37.8 19.6 [66:34]
b) 77 % 12.8 % [86:14] 77 % 12.8 % [86:14] 77 % 12.8 % [86:14] 77 % 12.8 % [86:14] (Distillate from example 2)	n-Pentane Benzene (63-80°C) Cyclohexane Toluene	46-48°C 84 h 70-72°C 72 h 90-92°C 25 h 120 °C 25 h	17.1 11.1 60.1 0.8 [99: 1] 1.8 14.6 57.9 14.3 [80:20] 2.4 10.0 65.5 11.3 [85:15] - 84.6 14.3 [86:14]
c) 6.3 % 59.3 % [ 9:91] 6.3 % 59.3 % [ 9:91] 6.3 % 59.3 % [ 9:91] (from example 3)	Benzene (63-80°C) Cyclohexane Toluene	70-72°C 78 h 90-92°C 78 h 120 °C 78 h	1.2 14.5 28.6 19.8 [59:41] 2.1 11.5 36.9 13.6 [73:27] 2.9 8.4 37.7 13.3 [73:27]
d) 13.4 % 80.6 % [14:86] 13.4 % 80.6 % [14:86] (from example 4)	Benzene (63-80°C) Toluene	70-72°C 72 h 120 °C 48 h	- 22.9 35.6 35.1 [50:50] 1.5 3.3 67.9 19.8 [77:23]

160x

4/13  
Table  
6

EXAMPLE 6

Manufacture of 5-ethylenedioxy-3B-H-isolongifolane (5a)

20 g purified ketale mixture from example 5b; (purity according to GLC: 5a (84.6 %), 5b (14.3 %) [86:14], were distilled once more for purification in a 1 m spinning band column. 2.8 g 5a as a light yellow oil were obtained, b.p.<sub>2mm</sub> 142 - 143 °C.

GLC: 5a (98 %), 5b (0,8 ) [99:1]

D 20/4 = 1,0510

n 20/D = 1,5051

GLC/MS: Conditions see example 2

5a Rt 42.94'

MS: m/e (%) = 264 (23, M<sup>+</sup>), 249 (9), 235 (19), 195 (20), 165 (23), 127 (42), 99 (100), 55 (10).

<sup>1</sup>H-NMR: see design 1

<sup>13</sup>C-NMR (CDCl<sub>3</sub>), Varian VXR-300): δ [ppm] = 21.86, 23.39, 26.79, 33.89 (CH<sub>3</sub>), 21.06, 25.75, 32.76, 35.89, 37.95, 61.84, 63.71 (CH<sub>2</sub>), 48.94, 52.48 (CH); 33.21, 37.67, 56.42, 112.23 (C).



EXAMPLE 7

Isolation of 5-ethylenedioxy-3 $\alpha$ -H-isolongifolane (**5b**)

1 g of raw ketal mixture from example 5d (purity according to GLC: **5a** (35.6 %), **5b** (35.1 % [1:1]) was purified by repeated (3 x) flash-chromatography.

Conditions of chromatography:

150 g silica gel 60, Grain size 0.04 - 0.063 mm, (Merck, Art.-No. 9385).

Solvent: Benzene / Ethyl acetate = 95 / 5

Weight: 1 g

Yield: 78 mg; GLC: **5a** (3 %), **5b** (90 %) [3:97]

GLC/MS: Conditions see example 2

**5b** Rt 44, 67'

MS: m/e (%) = 264 (9, M<sup>+</sup>), 249 (1), 235 (1), 221 (2), 191 (1), 149 (2), 127 (9), 99 (100), 55 (6), 41 (3).

<sup>1</sup>H-NMR: see design 2

<sup>13</sup>C-NMR (CDCl<sub>3</sub>), Varian VXR-300):  $\delta$  [ppm] = 25.51, 26.72, 26.93, 31.09 (CH<sub>3</sub>), 26.01, 30.41, 31.65, 36.90, 37.56, 61.38, 63.05 (CH<sub>2</sub>), 49.53, 56.89 (CH), 32.46, 40.99, 56.63, 111.78 (C).

CE  
440  
EXAMPLE 8

Manufacture of 5-(1'-Methylethylenedioxy)-isolongifolane  
6a/6b/6c/6d

440 g (2 mol) of purified ketone mixture 4a/4b from example 2;  
(purity according to GLC: 4a (77 %), 4b (12.8 %) [86:14], 760 g  
(10 mol) propylene glycol-1.2, 600 ml toluene, 2 g p-toluene sul-  
fonic acid were charged into a 4 l three-neck-roundbottom-flask  
with water separator. The mixture was stirred for 30 hours under  
reflux. After cooling to room temperature it was neutralized with  
~~sodium~~ <sup>sodium</sup> carbonate solution and water, dried above Na<sub>2</sub>SO<sub>4</sub> and the  
solvent was distilled at reduced pressure. 540 g of light brown  
raw product remained.

Distillation with a 15 cm Vigreux-column produced 298 g (53.6 %  
theor. yield) 6a/6b/6c/6d; b.p.<sub>2mm</sub> 158 - 162 °C).

GLC/MS: Conditions see example 2

Rt 41.11'

MS: m/e (%) = 278 (21, M<sup>+</sup>), 263 (19), 249 (40), 179 (41),  
141 (39), 113 (100), 83 (20), 55 (31).

Rt 42.03'

MS: m/e (%) = 278 (29, M<sup>+</sup>), 263 (22), 249 (55), 209 (40),  
179 (49), 141 (42), 113 (100), 83 (21), 55 (31).

P40

Rt 42,11'

L

MS: m/e (%) = 278 (23, M<sup>+</sup>), 263 (21), 249 (44), 209 (35),  
179 (47), 141 (39), 113 (100), 83 (21), 55 (34).

P40

Rt 42,47'

L

MS: m/e (%) = 278 (29, M<sup>+</sup>), 263 (21), 249 (51), 209 (37),  
179 (47), 141 (44), 113 (100), 83 (21), 55 (26).

Cl

#### EXAMPLE 9

Cl 40

Manufacture of 5-(1'-Ethyl-ethylenedioxy)-isolongifolane

I

7a/7b/7c/7d

PI

L

220 g (1 mol) purified ketone mixture **4a/4b** from example 2 (purity according to GLC: **4a** (77 %), **4b** (12.8 %) [86:15], 270 g (3 mol) 1,2-butandiol, 300 ml cyclohexane, and 1 g p-toluene sulfonic acid were charged into a 1 l three-neck-roundbottom-flask with water separator. The mixture was stirred for 50 hours. After cooling to room temperature it was then neutralized with <sup>sodium</sup> ~~sodium~~ carbonate solution and water and dried above Na<sub>2</sub>SO<sub>4</sub>. After distillation of the solvent at reduced pressure 328 g of light brown oil remained.

C

4/4 195 g (66.8 % theor. yield) **7a/7b/7c/7d**; b.p.<sub>2mm</sub> 152 - 157 °C as light yellow oil.

clwl GLC/MS: Conditions see example 2

p40 Rt 42,55'

L MS: m/e (%) = 292 (16, M<sup>+</sup>), 277 (15), 263 (37), 223 (27),  
193 (28), 155 (26), 127 (100), 83 (13), 55 (43).

p40 Rt 43,37'

L MS: m/e (%) = 292 (32, M<sup>+</sup>), 277 (25), 263 (56), 223 (48),  
193 (41), 155 (37), 127 (100), 83 (17), 55 (49).

p40 Rt 43,66'

L MS: m/e (%) = 292 (19, M<sup>+</sup>), 277 (19), 263 (42), 223 (45),  
193 (34), 155 (28), 127 (100), 83 (13), 55 (50).

p40 Rt 44,29'

L MS: m/e (%) = 292 (32, M<sup>+</sup>), 277 (24), 263 (57), 223 (43),  
193 (41), 155 (43), 127 (100), 83 (17), 55 (50).

cl EXAMPLE 10

cl40 Manufacture of 5-(1',2'-dimethyl-ethylene dioxy)-isolongifolane  
I 8a/8b/8c/8d

p1 220 g (1 mol) of purified ketone mixture 4a/4b from example 2  
L (purity according to GLC: 4a (77 %), 4b (12.8 %) [86:14]; 270 g  
(3 mol) 2,3-butandiol, 300 ml cyclohexane, and 1 g p-toluene sul-  
fonic acid were charged into a 1 l three-neck-roundbottom-flask

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c and stirred for 50 hours under reflux. After cooling to room temperature it has been neutralized with <sup>sodium</sup>~~sodium~~ carbonate solution and water and dried above  $\text{Na}_2\text{SO}_4$ . The solvent was distilled at reduced pressure. 275 g light brown raw product remained.

p Distillation with a 15 cm Vigreux-column produced 211 g (72.2 % theor. yield) **8a/8b/8c/8d**; b.p. 2.5 mm 158 - 162 °C as a light yellow oil.

p  
L D 20/4 = 1,0115

n 20/D = 1,4975

clwl GLC/MS: Conditions see example 2

p 40  
L Rt 39,69'

MS: m/e (%) = 292 (41,  $\text{M}^+$ ), 277 (25), 263 (57), 223 (50),  
193 (49), 155 (50), 127 (100), 83 (20), 55 (29).

p 40  
L Rt 40,14'

MS: m/e (%) = 292 (47,  $\text{M}^+$ ), 277 (30), 263 (63), 223 (59),  
193 (53), 155 (51), 127 (100), 83 (20), 55 (35).

p 40  
L Rt 42,76'

MS: m/e (%) = 292 (16,  $\text{M}^+$ ), 277 (14), 263 (28), 223 (28),  
193 (26), 155 (25), 127 (100), 83 (15), 55 (28).

p 40  
L Rt 43,36'

MS: m/e (%) = 292 (56, M<sup>+</sup>), 277 (40), 263 (91), 223 (78),  
193 (66), 155 (64), 127 (100), 83 (38), 55 (41).

cl  
clul  
EXAMPLE 11

Description of odours of ketals 5 to 8

P The olfactory qualities of the materials at 10 % in Ethanol have  
been evaluated by a group of experts using smelling strips.  
Their findings were as follows:

P 1  
L 5a/5b [86:14] from example 5b:

strong, sweet-woody, with a velvety-ambra accent and flowery  
aspects.

P 1  
L 5a from example 6:

strongly woody with a mossy ambra-accent and a fresh effect.

P 1  
L 5b from example 7:

woody, light flowery, with a softly earthy ambra note, a bit  
weaker than compound 5a.

P 1  
L 6a/6b/6c/6d (from example 8):

strongly woody, powdery, with a fresh ambra accent.

P 1  
L 7a/7b/7c/7d (from example 9):

dry, woody

23

1 8a/8b/8c/8d (from example 10):

strongly woody, with aspects of mossy, earthy and sweet-animal notes.

The odors of all compounds were found to be extremely longlasting and could be smelled after several weeks.

cl EXAMPLE 12

clvl Perfume base of a flowery-woody type

Oil of bergamot	7.5
Linalool	4.0
Phenyl ethyl alcohol	5.0
Benzyl acetate	2.0
T250X Citronellol	2.0
Hedione <sup>(R)</sup> (a)	10.0
Lyr <sup>(R)</sup> (b)	4.0
Hydroxycitronellal	2.5
Roseoxide 1 (c) 10 % in DPG	2.5
Hexyl cinnamic aldehyde, alpha	7.5
Patchouly Oil Indonesian	4.0
Iso-E-Super <sup>(R)</sup> (b)	2.0
Vetiveryl acetate	2.0
Brahmanol <sup>(R)</sup> F (c)	2.0
Benzcylsalicylat	2.0
cis-3-Hexenylsalicylat	1.0
Cedramber <sup>(R)</sup> (b)	1.0
Musk Xylene	1.0
Indole 10 % in DPG	0.5
Extract of Opoponax	0.5
Extract of Oakmoss 50 % in DPG	5.0
	68.0

(a) Firmenich

(b) IFF

(c) DRAGOCO

P The perfume base of the indicated formula presents a well balanced flowery-woody character which may be markedly amplified and harmonized by addition of 32 parts of 5a/5b (80:20).

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cl EXAMPLE 13

clol Perfume base of the fougère type

1260X

Oil of bergamot	18,0
Oil of Lavandin Super	15,0
Lilial <sup>(R)</sup>	10,0
p-anisaldehyde	3,0
Coumarin	5,0
Hexyl cinnamic aldehyde, alpha	20,0
Ambrinol epoxide 10 % in DPG	0,5
Ambroxan <sup>(R)</sup> (d) 10 % in DPG	1,0
Romaryl <sup>(R)</sup> (c)	10,0
Peppermint oil	<u>1,0</u>
	82,5

(c) DRAGOCO

(d) Henkel

P  
1/2 acn  
I  
The perfume base of the indicated formula shows a fresh herbal fougère odor. An addition of 7.5 parts **6a/6b/6c/6d** smoothes the composition and puts an accent on the ambra-woody note. Alternatively, an addition of 7.5 parts **8a/8b/8c/8d** also smoothes the composition but puts the accent on an animal woody aspect.

EXAMPLE 14

Coeur of the green flowery type

Oil of Galbanum ED	0.5
Eugenol	1.0
Methylionone-gamma	5.0
cis-3-Hexenylsalicylat	6.0
Benzyl acetate	8.0
Lignofix <sup>(R)</sup> (c)	5.0
Hedione <sup>(R)</sup> (a)	10.0
Bencylsalicylat	10.0
Hexyl cinnamic aldehyde, alpha	12.0
Phenyl ethyl alcohol	<u>15.0</u>
	72.5

(a) Firmenich

(c) DRAGOCO

The perfume oil of the indicated formula shows a harmonic flowery green character. Alternative addition of either 7.5 parts **5a/5b** or **7a/7b/7c/7d** produces a very desirable balancing in a very natural effect.

am We claim: